Catalysis Letters Vol. 107, Nos. 3–4, March 2006 (© 2006)
DOI: 10.1007/s10562-005-0009-3

A green synthesis of 2-ethylanthraquinone from 2-(4′-ethylbenzoyl) benzoic acid over H-Beta zeolite

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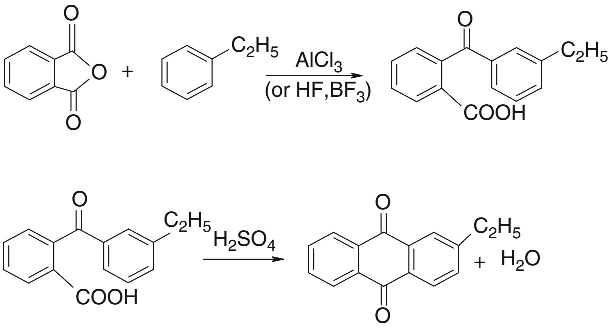
Received 8 August 2005; accepted 13 December 2005

The dehydration of 2-(4′-ethylbenzoyl) benzoic acid (BE acid) for the synthesis of 2-ethylanthraquinone (2-EAQ) has been studied over solid acid catalysts. Among the catalysts tested, a H-Beta zeolite, which was modified by dilute HNO_3 solution, exhibited high catalytic performances. A 96.7% yield of 2-EAQ was achieved in our study in a batch reactor. The influences of various parameters, such as reaction temperature and time, the weight ratio of BE acid to H-Beta zeolite were investigated in detail.

KEY WORDS: Dehydration; 2-(4′-ethylbenzoyl) benzoic acid; 2-ethylanthraquinone; H-Beta.

1. Introduction

2-Ethylanthraquinone (2-EAQ) is an important intermediate for the synthesis of hydrogen peroxide, pharmaceuticals, pesticides, and dyes. With the increasing demands for hydrogen peroxide in the international market, it needs to increase the production of 2-EAQ. The traditional manufacture process of 2-EAQ consists of two reaction steps (Scheme 1).



Scheme 1

The first step has been carried out in the presence of $AlCl_3$ [1] or HBF_4 [2], and the second step is the dehydration of 2-(4′-ethylbenzoyl) benzoic acid (BE acid), which is commonly catalyzed by concentrated H_2SO_4[2,3] or oleum [1–3]. In the traditional process, a large amount of waste acid is generated, which is hazardous to environment, human beings and production system. Therefore, an alternative process, which is environmentally benign is desired. Using solid acid catalysts may be a very promising way for the synthesis of 2-EAQ considering their activity, selectivity and re-usability.

Beta zeolite, which possesses 3-dimensional 12-membered-ring pore openings, is an intergrowth hybrid of two distinct but closely related structures that have tetragonal and monoclinic symmetry [4]. Due to its special pore system and surface acidity, Beta zeolite is a candidate for the synthesis of many fine-chemicals. The catalytic properties of Beta zeolite in various reactions, for example, the synthesis of anthraquinone [5,6], the cracking of paraffins [7], the isomerization of *n*-heptane [8] and *n*-hexane [9], the disproportionation and transalkylation of toluene and C_9 aromatics [10], the alkyl aromatics transalkylation [11], benzene alkylation with long-chain olefins [12], and the hydration of propene to isopropanol [13], etc., have been investigated. However, there are no reports about the dehydration of BE acid into 2-EAQ over Beta zeolite catalyst.

In this paper, the dehydration of BE acid into 2-EAQ over zeolite catalyst, including H-Beta, H-Y and H-ZSM-5 catalysts, was carried out in a batch reactor. The influences of reaction parameters, such as reaction temperature and time, the weight ratio of BE acid to H-Beta zeolite were investigated.

2. Experimental

2.1. Catalyst preparation

A H-Y ($SiO_2/Al_2O_3 = 6$) catalyst was prepared by calcining NH_4-Y (obtained from the Chinese Changling Catalysis Group) at 550 °C for 4 h in air. A H-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 80$) and a H-Beta zeolite ($SiO_2/Al_2O_3 = 22$) were acquired by treating the sodium form

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zeolites (provided by Department of Catalysis Chemisty and Engineering, Dalian University of Technology) with 0.4 mol/L NH_4NO_3 at 80 °C for 2 h in air. The exchange process was repeated twice, and the obtained catalysts were calcined at 550 °C for 4 h.

The H-Beta zeolite ($SiO_2/Al_2O_3 = 22$) was dealuminated by HNO_3 solution with different concentration, then the H-Beta zeolites with different SiO_2/Al_2O_3 ratios were obtained. The typical preparation was as followings: the H-Beta ($SiO_2/Al_2O_3 = 22$) (10 g) was added to HNO_3 solution (100 ml) with different concentration, and the mixture was stirred at 80 °C for 2 h. This operation was repeated twice. The obtained solid was washed and dried at 100 °C for 12 h, then calcined at 550 °C for 4 h. The concentration of HNO_3 solution used in the preparation of catalyst and the SiO_2/Al_2O_3 molar ratios of H-Beta were shown in table 1.

2.2. *Catalyst characterization*

X-ray powder diffraction patterns of the samples were recorded using a Rigaku D/max-2400 apparatus using $CuK\alpha_1$ radiation. XRF (SRS3400 X) was used to determine the composition of the H-Beta zeolites (SiO_2/Al_2O_3 molar ratio). NH_3-TPD experiments were performed on a conventional set-up equipped with a thermal conductivity detector (CHEMBET 3000). FT-IR of pyridine adsorption (EXUINOX 55) was used to measure the acid nature.

2.3. *Catalytic testing*

The dehydration of BE acid was carried out in a glassware reactor operating in the batch mode under the atmospheric pressure. In a typical experiment, the solid BE acid was first heated to the required temperature and was changed into liquid in the reactor, then H-Beta zeolite catalyst was added into the reactor with continuous magnetic stirring. The agitation speed was 600 rpm. After the reaction, 1,4-diethylene dioxide was added in the reaction mixture to dissolve both product and reactant. The product was analyzed on a liquid-chromatogram (Agilent 1100) equipped with a ZORBAX SB-C18 (250 mm×4.6 mm) column at room temperature. The mobile phase was a mixture of H_2O and CH_3OH with a flow-rate of 1.000 ml/min at UV 257 nm. The retention time was approximately 25 min. The calibration curve was linear for BE acid ($r = 0.9994$) and 2-EAQ ($r = 0.9963$).

Table 1
The preparation conditions of H-Beta zeolite

Sample no.	1	2	3	4
The concentration of HNO_3 solution (mol/L)	0.5	1.0	2.0	5.0
The SiO_2/Al_2O_3 molar ratio of H-Beta	107	162	232	702

3. Results and discussion

3.1. *The dehydration of BE acid over different zeolite catalysts*

The dehydration of BE acid has been carried out over three acidic zeolites with different structures, H-Beta, H-Y, H-ZSM-5, respectively. The results were shown in table 2. H-Beta (22) zeolite is the most active catalyst both in the terms of conversion and selectivity. While over the H-ZSM-5 (80) or H-Y (6) catalyst, both the conversion of BE acid and the selectivity to 2-EAQ are very low. The pores of the interconnected channel architecture of H-Beta (22) allow the easier diffusion of the product than the supercages structure architecture of H-Y (6). For the H-ZSM-5 (80) catalyst, the reaction probably occurred on the external surface of the catalyst due to its small pore size. Moreover, over H-ZSM-5 (80) or H-Y (6) catalyst, there are anthraquinone and methylanthraquinone in the products. This shows that demethylation and deethylation happen during the dehydration of BE acid into 2-EAQ.

From the above results it can be seen that the H-Beta zeolite is a more effective catalyst for the dehydration of BE acid into the 2-EAQ. Hence, H-Beta zeolite is used as the catalyst in the following study.

3.2. *Dehydration of BE acid over H-Beta zeolite catalysts*

3.2.1. *The effect of SiO_2/Al_2O_3 ratio of H-Beta zeolite on the dehydration of BE acid*

Figure 1 is the XRD spectra of the H-Beta with different SiO_2/Al_2O_3 molar ratios. It can be seen that all of the samples exhibit the typical diffraction peaks of Beta zeolite ($2\theta = 7.62°$ and $22.50°$), and there is no impurity phase. This shows that the framework is not damaged by the treatment with HNO_3 solution.

Figure 2 is the NH_3-TPD curves of H-Beta with different SiO_2/Al_2O_3 molar ratios. It can be found that the amount of total acid sites decreases, when the SiO_2/Al_2O_3 molar ratio of H-Beta zeolite increases. The decrease in the amount of weak acid is more than that in the amount of strong, and the NH_3-TPD peaks shift to lower temperature. This demonstrates that the amount and the strength of acid sites decrease with the increase in the SiO_2/Al_2O_3 molar ratio.

Figures 3, 4 and 5 is the FT-IR spectra of pyridine desorbed on H-Beta with different SiO_2/Al_2O_3 molar ratios at 150, 300, 450 °C, respectively. It can be seen clearly that the concentration of Brønsted acidity sites decreases as the SiO_2/Al_2O_3 molar ratio increases in figures 3 and 4. However, the concentration of Brønsted acidity sites does not decrease with the increasing of SiO_2/Al_2O_3 molar ratio in figure 5. The relative concentration of Brønsted acidity sites and Lewis acidity sites in zeolite is determined using the relation $B/L = (A_B/A_L)\ (\varepsilon_L/\varepsilon_B)$, where A_B/A_L is the absorbance ratio and $\varepsilon_L/\varepsilon_B$ is the extinction coefficient ratio. It is reported that$\varepsilon_L/\varepsilon_B$ value is 1.5 for samples with a $SiO_2/$

Table 2
The dehydration of BE acid over different zeolite catalysts

Catalyst	Pore size (nm)	Conversion of BE acid (mol %)	Production distribution (mol %)				Yield of 2-EAQ (mol %)
			AQ	MAQ	2-EAQ	Others	
H-Y (6)	0.74	3.5	1.9	73.6	18.4	6.1	0.6
H-ZSM-5 (80)	0.56×0.53	6.1	5.7	76.3	5.6	15.1	0.9
H-Beta (22)	0.75×0.67	62.8	0.4	5.4	93.1	1.1	58.5

Reaction conditions: BE acid/catalyst = 3.5 (g/g), reaction temperature = 250 °C, reaction time = 1.5 h, reaction pressure = 1 atm, AQ = anthraquinone, MAQ = methylanthraquinone.

Al_2O_3 ratio >15 [14]. The B/L ratios are shown in table 3.

From table 4, it can be seen that the SiO_2/Al_2O_3 molar ratio has a great effect on the conversion of BE acid and the selectivity to 2-EAQ. With the increase in the SiO_2/Al_2O_3 molar ratio, both the conversion of BE acid and the selectivity to 2-EAQ first reach the highest value, then decrease. Over the H-Beta (107) catalyst, the

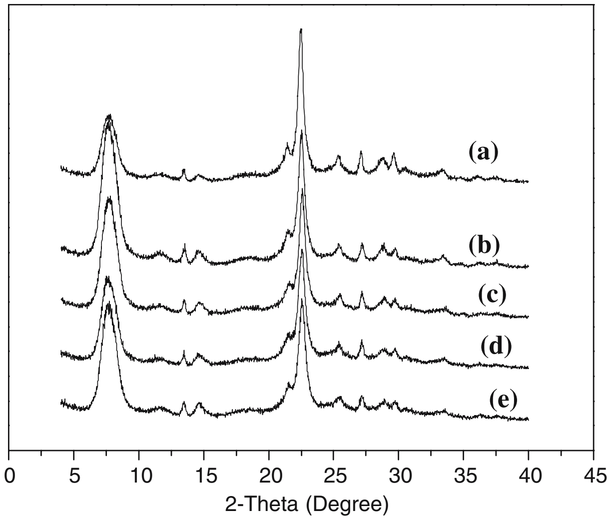

Figure 1. XRD patterns of H-Beta with different SiO_2/Al_2O_3 molar ratios, (a) 22 (b) 107 (c) 162 (d) 232 (e) 702.

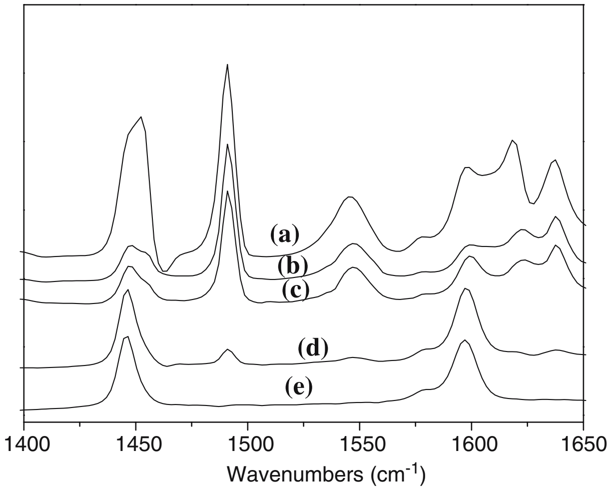

Figure 3. FT-IR spectra of pyridine desorbed of H-Beta with different SiO_2/Al_2O_3 molar ratios, (a) 22 (b) 107 (c) 162 (d) 232 (e) 702. The pyridine desorbed temperature is 150 °C.

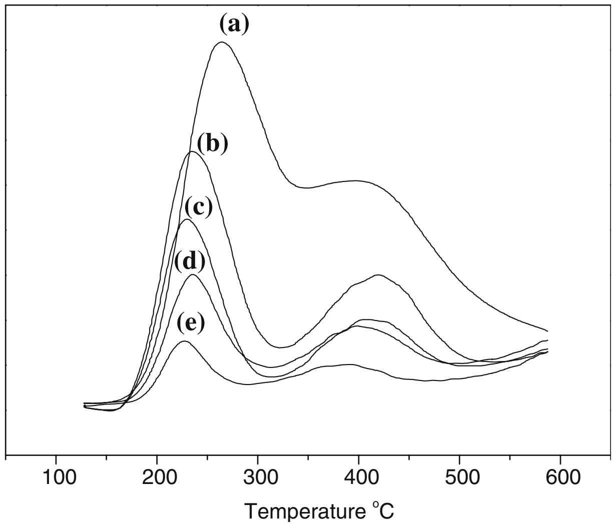

Figure 2. NH_3-TPD curves of H-Beta with different SiO_2/Al_2O_3 molar ratios, (a) 22 (b) 107 (c) 162 (d) 232 (e) 702.

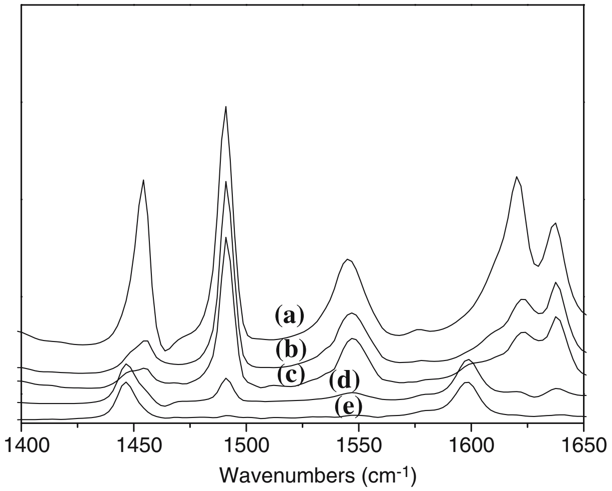

Figure 4. FT-IR spectra of pyridine desorbed of H-Beta with different SiO_2/Al_2O_3 molar ratios, (a) 22 (b) 107 (c) 162 (d) 232 (e) 702. The pyridine desorbed temperature is 300 °C.

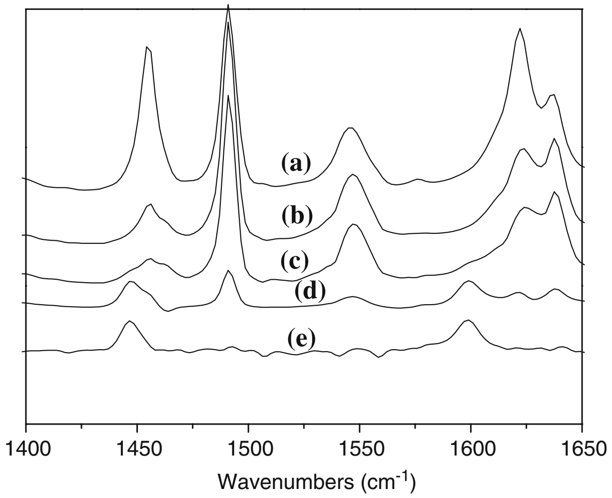

Figure 5. FT-IR spectra of pyridine desorbed of H-Beta with different SiO_2/Al_2O_3 molar ratios, (a) 22 (b) 107 (c) 162 (d) 232 (e) 702. The pyridine desorbed temperature is 450 °C.

conversion of BE acid is 85.9% and the selectivity to 2-EAQ is 95.9%. From figure 2, it can be seen that the amount of the total acid site of the H-Beta (22) is the most compared with other H-Beta zeolites, which is not in agreement with its activity. From tables 3 and 4, it can be seen that H-Beta (107) exhibits the highest catalytic activity, while H-Beta (162) has highest B/L ratio, there is not a proportional relationship between the catalytic activity and the B/L ratio of H-Beta catalyst. The research work is in study.

The above results show that the H-Beta (107) zeolite catalyst is an effective catalyst in the dehydration of BE acid. Therefore, H-Beta (107) zeolite is used as the catalyst to investigate the effect of reaction conditions.

3.2.2. Effect of the reaction conditions

The effect of reaction temperature on the conversion of BE acid and the selectivity to 2-EAQ over the H-Beta zeolite (107) was first investigated in the range of 242–300 °C, which is shown in figure 6. The conversion of BE acid increases rapidly with the increase of reaction temperature before 260 °C. At 242 °C, the conversion of BE acid is only 57.9%, while the conversion of BE acid reaches 98.3% at 260 °C. From figure 6, it can be seen that the selectivity to 2-EAQ changes slightly with the increasing of reaction temperature. The selectivity to 2-EAQ keeps at about 95.0%, the by-products is mainly anthraquinone and methylanthraquinone. Therefore, the suitable temperature is in the range of 260–280 °C in the dehydration of BE acid over H-Beta zeolite (107).

Figure 7 shows the influence of reaction time on the conversion of BE acid and the selectivity to 2-EAQ over H-Beta (107). It can be seen that the reaction time has a little influence on the selectivity to 2-EAQ, while the conversion of BE acid increases rapidly with the reaction time before 1.5 h. When the reaction time is 1.5 h, the conversion of BE acid reached 99.5%, and the selectivity to 2-EAQ reached 97.2%. Hence, the suitable reaction time is 1.5 h.

Table 3
Comparison of acid sites and B/L ratios determined by Pyridine-IR for different H-Beta

Catalyst	Temperature (°C)								
	150			300			450		
	A_B	A_L	B/L	A_B	A_L	B/L	A_B	A_L	B/L
H-Beta (22)	1.46	3.46	0.63	1.54	1.77	1.32	0.72	1.18	0.92
H-Beta (107)	1.00	0.80	1.88	1.08	0.53	3.06	0.84	0.42	3.00
H-Beta (162)	0.94	0.75	1.88	0.84	0.33	3.82	0.73	0.31	3.53
H-Beta (232)	0.14	1.25	0.17	0.10	0.57	0.26	0.14	0.30	0.70
H-beta (702)	0.05	1.07	0.07	0.02	0.41	0.07	0.07	0.22	0.48

B/L is calculated by the equation of $1.5\times(A_B/A_L)$, where A_B/A_L is the aborbance ratio [14].

Table 4
The dehydration of BE acid over H-Beta with different SiO_2/Al_2O_3 ratios

Catalyst (SiO_2/Al_2O_3)	Conversion (%)	Production distribution (%)				Yield of 2-EAQ (%)
		AQ	MAQ	2-EAQ	Others	
H-Beta (22)	62.8	0.4	5.4	93.1	1.1	58.5
H-Beta (107)	85.9	0.5	2.5	95.9	1.1	82.4
H-Beta (162)	77.4	0.8	3.9	93.8	1.5	72.6
H-Beta (232)	52.7	0.6	1.1	85.0	13.3	30.8
H-Beta (702)	32.9	1.2	21.4	75.0	2.5	24.7

Reaction conditions are the same as in Table 1.

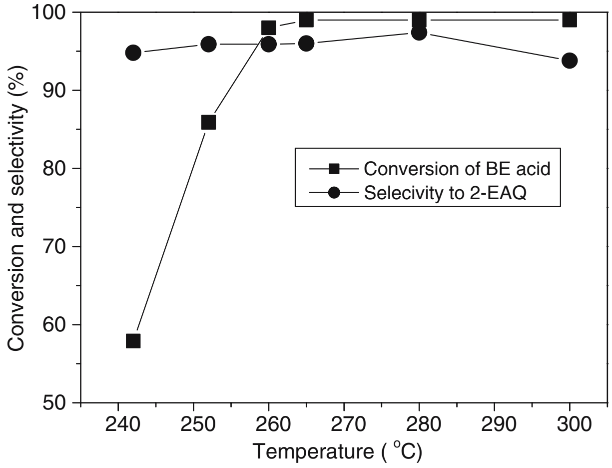

Figure 6. Effect of reaction temperature on the conversion of BE acid and the selectivity to 2-EAQ. Notes: The weight ratio of BE acid to H-Beta (107) zeolite is 3.5 g/g and the reaction time is 1.5 h.

Figure 8 is the effect of the weight ratio of BE acid to H-Beta zeolite (107) on the conversion of BE acid and the selectivity to 2-EAQ. It can be seen that the weight ratio of BE acid to H-Beta zeolite (107) also has a great effect on the conversion of BE acid and a slight effect on the selectivity to 2-EAQ. When the reaction time is 1.5 h, the weight ratio of BE acid to H-Beta zeolite is 3.5 at 265 °C, the conversion of BE acid can reach 99.5%. However, the conversion of BE acid is only 84.4%, when the weight ratio of BE acid to H-Beta zeolite (107) is 5. It is due to the decrease in the amount of the active sites as the weight ratio of BE acid to H-Beta zeolite increases. When the weight ratio of BE acid to H-Beta zeolite (107) reaches 3.0, little change in conversion of BE acid and the selectivity to 2-EAQ was observed. Therefore, the suitable ratio of BE acid to H-Beta zeolite is 3.0–3.5.

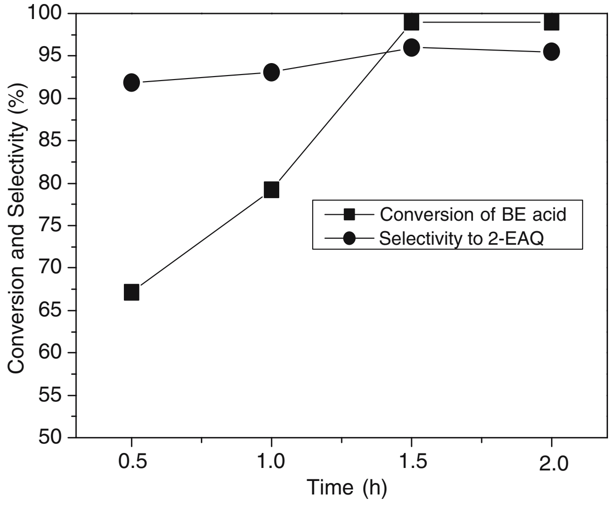

Figure 7. Effect of reaction time on the conversion of BE acid and the selectivity to 2-EAQ, Note: The temperature is 265°C and the weight ratio of BE acid to H-Beta (107) zeolite is 3.5 g/g.

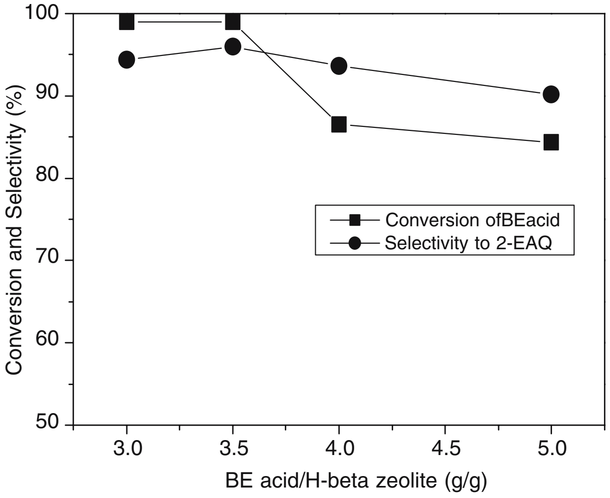

Figure 8. Effect of weight ratio of BE acid to H-Beta (107) on the the conversion of BE acid and selectivity to 2-EAQ (the reaction time is 1.5 h and the temperature is 265 °C).

By optimizing the catalyst preparation and reaction parameters, a selectivity to 2-EAQ as high as 97.2% is achieved.

4. Conclusions

The dehydration of BE acid has been investigated over different zeolites, such as H-Beta, H-Y and H-ZSM-5. The optimal reaction conditions over H-Beta (107) are BE acid to H-Beta zeolite weight ratio 3.0–3.5, reaction temperature 260–280°C, reaction time 1.5 h. The conversion of BE acid can reach 99.5%, and the selectivity to 2-EAQ is up to 97.2%. These results indicate that the H-Beta zeolite is an environmentally friendly catalyst alternative to the concentrated H_2SO_4 or oleum for the dehydration of BE acid reaction.

Acknowledgement

This project was sponsored by the program for New Century Excellent Talents in University in China.

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